Effect of capping on doped core-shell ZnS quantum dots

SYNOPSIS

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INTRODUCTION

Semiconductor quantum dots (QDs) exhibit size dependent properties[1-8]. Since these nano quantum dots have very high surface to volume ratio so surface defects play an important role in their study. The earlier approach for the synthesis of nanoparticles involves chemical or physical attrition from bulk into objects of desired sizes and shapes (e.g. mechanical milling, ion implantation, etc.), and is referred as the 'top-down' approach. Apart from the 'top-down' approach, other one is a process universal in nature, involving the assembly of materials from molecular levels to form micro or macro-sized shapes and structures, often referred as 'bottom-up' approach or 'self-assembly' [8]. Wet chemical synthesis involving colloids is the most energy efficient 'bottom up' technique for the synthesis of nanoparticles. The advantages of the Chemical synthesis is to produce size-controlled, un-agglomerated nanoparticles. The tunability of the properties of nanoparticles by controlling their size may provide an advantage in formulating new composite materials with optimized properties for various applications. But applications of these materials are restricted due to different non–radiative relaxations pathways [6]. One important non radiative relaxation is surface related defects. Most of the physical or chemical properties exhibited by these nanoparticles are due to their crystallites. Further growth in their size is due to agglomeration of these crystallites to form primary particles. If this growth of particles is not controlled, then due to Ostwald ripening and Vander-Waals interactions between particles, they may agglomerate and settle down [6-8]. This agglomeration can be arrested by either stabilizing them electrostatically or by inducing steric hindrance at appropriate stage(s) to achieve size selective synthesis during precipitation reaction.

Electrostatic stabilization involves the creation of an electrical double layer arising from ions adsorbed on the surface and associated counter ions that surround the particle in the dispersing media. Thus, if the electric potential associated with the double layer is sufficiently high, columbic repulsion between the particles will prevent their agglomeration. Steric hindrance can be achieved by the adsorption of large molecules such as polymers on the surface of the particles.To control the growth one can use different organic and inorganic capping agents to passivate the free QDs. To control the growth of nanoparticles organic stabilizers (polymers) e.g. polyethylene oxide (PEO),

poly (N-vinyl-2pyrroledone) (PVP), polyvinyl caracole (PVK), mercaptoethanol, thiophenol, thiourea , SHMP, sodium polyphosphate, etc. can be added during the wet chemical synthesis for capping [12-19]. Such materials have applications in luminescent devices, light emitters, phosphors optical sensors etc. [9-11]. Recently due to advancement in luminescent nanocrystals by successful capping which results in fluorescent labeling by semiconductor QDs for biological detection and tagging has demonstrated its application in many fields. Capping causes noticeable change in properties of nanoparticles.

Core-shell type composite quantum dots exhibit novel properties making them attractive from both experimental and technological point of view [9]. Nanoshells, which are thin coatings deposited on core particles of different material have gained considerable attention. These materials show novel properties which are different from their single-component counterpart. Simply by tuning the core to shell ratio, the properties can be altered. It is now possible to synthesize these nanostructures in desired shape, size and morphology with new emerging techniques. They can be prepared with customized properties such as increased stability, surface area, magnetic, optical and catalytic properties. Monodispersed colloids have attracted a lot of attention since a long time because of their novel properties and potential applications [9-10]. Nano shell particles constitute a special class of nano composite materials. They consist of concentric particles, in which particles of one material are coated with a thin layer of another material using specialized procedures [9]. Nanoshell particles are highly functional materials with tailored properties, which are quite different than either of the core or of the shell material. Indeed, they show modified and improved properties than their single component counterparts or nanoparticles of the same size. Therefore, nano shell particles are preferred over nanoparticles . Their properties can be modified by changing either the constituting materials or core-to-shell ratio [9]. The term nanoshell is used specifically because thickness of the shell is ca 1–20 nm. Properties of shell materials(metal or semiconductor) having thickness in nanometers, become important when they are coated on dielectric cores to achieve higher surface area. Sometimes they are referred as core shell or core@shell particles also [9]. Thicker shells can also be prepared, but their synthesis is restricted mainly to achieve some specific goal, such as providing thermal

stability to core particles. As it is not possible to synthesize all the materials in desired morphologies, synthesis of nanoshells can be useful for creating novel materials with different morphologies. These materials can be of economic interest also, as precious materials can be deposited on inexpensive cores. By doing so, expensive material is required in lesser amount than usual. These particles are synthesized for a variety of purposes like providing chemical stability to colloids enhancing luminescence properties, engineering band structures, biosensors drug delivery [9-11] etc. Usually dielectric materials such as silica and polystyrene are commonly used as core because they are highly stable. They are chemically inert and water-soluble; therefore they can be useful in biological applications. Nanoshell particles can be synthesized in a variety of combinations such as (core-shell) dielectric–metal, dielectric–semiconductor, dielectric-dielectric, semiconductor–metal, metal–metal, semiconductor–semiconductor, semiconductor–dielectric, metal– dielectric, dye–dielectric, etc. [9]. Core shell particles can be assembled and further utilized for creation of another class of novel materials like colloidal crystal or quantum bubbles. It is indeed possible to create unique core shell structures having multi shells. Multishell particles can be visualized as core particles having a number of shells around them. Core particles can be coated with a shell to obtain a single nano shell. Further, these combinations of core and shell can be repeated again to get multishells. By choosing different combinations of core and shell these structures show tunable optical properties from the visible to infrared region of the electromagnetic spectrum.

REVIEW OF LITERATURE

In order to gather information about the work done on the core-shell nanostructures of ZnS, literature survey was done in detail:

Kumbhojkar et al. [12] have synthesized ZnS (QDs) using wet chemical routes with 1-thioglycerol, thiophenol and mercaptoethanol to passivate the nanoclustors. Thiophenol and mercaptoethanol were used to synthesize the QDs at room temperature. Here size selective precipitation was carried out to obtain remarkably narrow size distribution of QDs. They have observed optical absorption spectra of ZnS nanoclusters passivated with

above mentioned organic ligands and uncapped ZnS QDs. Chung G. Jaehun et al. [13] have found that the luminescence, shape, and stability of ZnS nanoparticles in ethanol are enhanced by capping the surface with (3-mercaptopropyl) trimethoxy silane (MPS) or by treating the surface with SiO_2. While MPS forms an exterior network to encapsulate the ZnS surface, SiO_2 surrounds ZnS nanoparticles to smoothen the surface. T. Kubo et al.[14] have found modification of ZnS:Mn nanocrystal suspension by a surfactant with a phosphate or carboxyl group. They have found increase in photoluminescence intensity and its quantum efficiency due to d–d transition of Mn^{2+} ions through two routes of energy transfer: (1) ZnS-Mn^{2+} and (2) ZnS-phosphate or carboxyl groups-Mn^{2+}. N Karar et al. [15] have prepared ZnS: Mn in nanocrystalline form by a chemical method using PVP as a capping agent. They have varied Mn concentration over whole solid solution limit in ZnS, i.e. from 0 to 40%. K. Manzoor et al. [16] have studied multi-colour emitting doped ZnS nanocrystals capped with pyridine (P-ZnS) or polyvinyl pyrrolidone (PVP-ZnS) synthesized by wet chemical methods. The photoluminescence studies show that the dopant related emission from P-ZnS nanocrystals are caused by the energy transfer from band-to-band excitation of the host lattice. However, in the case of PVP capped ZnS, considerable enhancement in the emission intensity was observed and the corresponding excitation spectra appeared to be broadened due to the presence of multiple excitation bands with peak maxima at 235, 253, 260, 275, and 310 nm. The presence of PVP related energy bands in the excitation spectrum indicates the process of energy transfer from the surface adsorbed PVP molecules to dopant centers in ZnS nanocrystals. This study brings out a heterogeneous sensitizer-activator relation between organic surface adsorbate and doped semi conducting nanocrystals. Ghosh. et al. [17] have synthesized polyvinyl pyrrolidone (PVP) encapsulated ZnS nanoparticles. They added calculated quantity of zinc acetate, thiourea and PVP and dissolved it in N, N-dimethyl form amide (DMF) medium with constant stirring of 150 rpm. Their observed TEM image of ZnS nanoparticles which suggests the effect of capping. It represents PVP capped ZnS nanoparticles are mono dispersed in nature. Their size is 2-3 nm which matches with XRD results. While uncapped nanoparticles on the other hand are agglomerated and are larger than capped one's. This illustrates the use of PVP as capping agent. Blue shift of absorption edge compared to bulk ZnS clearly explained quantum confinement effect of ZnS nanoparticles. H.C. Warad et al. [18] have reported the

synthesis of redispersible zinc sulphide nanophosphor doped with manganese passivated with biocompatible chitosan molecules. The presence of biocompatible capping agent, chitosan, makes it suitable for bio-labels (markers). Benjamin Gilbert et al. [19] have combined real space pair distribution function (PDF) analysis of nanoparticle structure with particle size analysis and FTIR to reveal that the nature of surface solvent or ligand interactions can affect the interior crystallinity of nanoparticles. The availability of particles with a range of crystallinity provides a model system in which it is possible to determine the interior disorder affects of nanoparticle, where properties such as mechanical stiffness and fluorescent quantum yield are affected. PDF analysis showed that samples of ZnS nanoparticle with similar mean diameters (3.2 – 3.6 nm) but synthesized and treated differently possess a dramatic range of interior disorder. H. C Warad et al. [20] have synthesized quantum dots of manganese doped ZnS by a simple precipitation reaction using aqueous route resulting in primary particle sizes of 60–80 nm. The nanoparticles were sterically stabilized using polyphosphates of sodium namely sodium tripolyphosphate (STTP) and sodium hexametaphosphate (SHMP). It was established that SHMP was a superior capping agent than STTP. It was observed that the particle sizes are dependant on the amounts of stabilizing agents (SHMP) used during synthesis thus making it possible to alter the particle sizes by changing the concentrations of stabilizing agents used during synthesis. Dongjin Kim et al. [21] have studied optical properties of ZnS: Cu nanocrystals using sodium polyphosphate (SPP) as a capping agent. ZnS nanoparticles had the cubic structure (β-ZnS), and the crystal structure was not changed with the input of SPP. The particle morphology was spherical, and grain size was decreased and particle agglomeration was reduced with an increase of SPP input amount. The position of UV absorption edge was found to depend upon the SPP input amount, and it was decreased from 340 to 280 nm with the increase of SPP from 0.0 to 1.89 g, clearly showing the remarkable blue-shift phenomenon. Photoluminescence (PL) intensities were also dependent upon the amount of capping agent, and the highest PL intensity was obtained for the sample capped with SPP (1.13 g). PL emission wavelength was also blue-shifted, and it was decreased from 518 to 462 nm with the increase in SPP from 0.0 to 1.89g [21]. The properties such as excitonic binding energy, absorbtion edge, excitonic emission, particle size etc. changes with the slight variations in nature of the capping agents, molar concentration of capping agent/Zn/S/dopants, nature of the

dopants. The particle morphology was spherical, and grain size was decreased and particle agglomeration was reduced with an increase of capping input amount. The position of UV absorption edge was found to depend upon the capping input amount, and it decreases with increase of capping input which clearly shows the remarkable blue-shift phenomenon. This change in properties is mainly due to the quantum confinement effects observed in the band gap of the ZnS. So it is clear that effect of capping on stability of nanostructures is required. Kuldeep S. Rathode et al. have studied the structural and optical characterization of chemically synthesized ZnS nano particles.Different sized nanoparticles are possible to produce using simple chemical metjod with out using capping agent. XRD and optical band gap data have to be obtained to confirm nano size of the particle. It is observed that the particle size depends on molar concentration of reactant solution[22]. A decrease in formation rate of nanoparticles gives rise to a larger final particle size for all the studied synthesis conditions. Chemical reaction rate affects both nucleation and growth process. It has been shown that nucleation and growth take place simultaneously when the chemical reaction is slow. In addition, the ripening contribution to the growth is larger as the chemical reaction is slower. As the particle size depend upon the molar concentration of reactant solution, a decrease in the size of particle is observed with the increase of molar concentration of reactants. Jyoti. P Borah etal reported in their paper that ZnS nanoparticles of different crystalline sizes have been synthesized by chemical route[23]. The particle size is controlled by stirring rate, temperature of the solution, pH and time of stirring. The structural and optical characterization of the samples observed by XRD,TEM,UV-VIS spectrophotometer and PL shows formation of ZnS nanoparticle., having size between 5-7nm. The optimum pH value for minimum size is found to be 1.4 and PVA:ZnCl2 ratio is found to 5:1 in our observation. Manoj Sharma etal worked on the Core-Shell ZnS nanocrystals that have been synthesized using chemical precipitation method. Optical and morphological measurements on ZnS nanoclusters have been carried out to investigate the effect of capping on ZnS nanoparticles. XRD results show the crystallite size to be from 1.5-2.5 nm depending upon the peaks. TEM results shows uncapped agglomerated nanoparticles as well as PVP capped ZnS particles. It is clear from the TEM that PVP capping forms core-shell nanostructures and they also avoid agglomeration of the particles. Band gap of PVP capped ZnS nanoparticles is found to increase in comparison with uncapped ZnS

nanoparticles indicating quantum size effects [24]. The bandgap data from UV-visible reflectance and excitation are in correlation with each other. Increase of intensity in case of capped ZnS compared to uncapped ZnS shows better surface passivation. In conclusion PVP layer leads to the transfer of energy to the possible transition levels in ZnS. It means we can synthesize highly efficient doped ZnS using this transfer mechanism.

GAPS IN THE STUDY

1. It is clear from the review of literature that the properties of organically capped doped and undoped ZnS nanostructures are very sensitive to preparation conditions such as pH, temperature, molar concentration of the precursors, synthesis techniques, nucleation atmosphere, lattice mismatching etc. For the functionalization of any type of nanostructures for industrial applications, the results should be reproducible and stable. It is very important from the industrial point of view that one should study the various parameters of doped core-shell ZnS quantum dots with respect to time domain.

2. Steric hindrance and electrostatic stabilization are two different approaches to passivate nanostructures. The properties of any type of core-shell nanostructures depend on the type of capping agent whether it is organic and inorganic. The properties vary with the change in nature and amount of capping agent . It is also very important to study variable capping agents, their concentration and other synthesizing parameters on the behaviour of ZnS quantum dots.

3. Very less work is done on the study of core-shell nanostructures involving doped ZnS. Doping in semiconductors leads to the generation of optoelectronic material. But in the case of nanomaterials, defects play a major role. To use this material effectively surface passivation is required. That is why more studies should be conducted on ZnS with different capping agents.

OBJECTIVES

1. To synthesize doped core-shell ZnS quantum dots using chemical precipitation technique.

2. To study the effect of organic capping on the optical (Band Gap, Photoluminescence) and morphological (shape, size and structure) properties of ZnS Quantum dots.

3. To characterize the capped and uncapped ZnS core-shell nanostructures by using XRD, TEM, SAED, Photoluminescence spectroscopy, UV-vis absorption and Reflectance Spectroscopy, EDS etc.

METHODOLOGY

1. Doped ZnS core-shell quantum dots will be fabricated using chemical precipitation technique..

2. Organic capping agents which will be tried are PVP, Mercaptoethanol, Thioglycerol etc.

3. Capped and uncapped core-shell quantum dots will be characterized by using XRD, TEM, SAED, Photoluminescence spectroscopy, UV-visible absorption and reflectance spectroscopy, EDS, AAS etc.

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